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Effects of Internal Electron Donor on the Active Center Distribution of 1-Hexene Polymerization with MgCl$_2$-supported Ziegler-Natta Catalysts

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It has become a common recognition that the broad molecular weight distribution (MWD), chemical composition distribution (CCD) and steroesequence distribution of polyolefin synthesized with heterogeneous Ziegler-Natta catalysts are closely related with the distribution of their multiple active centers. [1] Different type of electron donors have been introduced into MgCl$_2$-supported titanium catalysts to improve their stereoselectivity. In doing so, the internal donor (ID) is believed to coordinate preferentially to Mg of the (110) cuts, selectively poison poorly stereoselective active sites, or transform certain types of aspecific sites into highly stereospecific ones. [2] However, there are still no enough experimental data on the changes of active center distribution made by the internal donors. A detailed investigation into these changes may greatly improve our knowledge of the roles played by internal donor.

In this work, three kinds of MgCl$_2$/TiCl$_4$/ID type Ziegler-Natta catalysts (Cat-1, Cat-2, Cat-3) were studied for 1-hexene polymerization, in which Cat-1 contains no ID, Cat-2 contains diethyl phthalate (DEP) as ID, and Cat-3 contains anisole as ID. [3] The polymerizations were quenched using cinnamoyl chloride, and the polymers were fractionated into a series of fractions by precipitation fractionation. The number of active centers in each fraction was determined by measuring the cinnamoyl group connected to the propagation chains in the quenching reaction. [4] With these data, the propagation rate constants of the active centers in different fractions were also determined. In this way, it is possible to depict the active center distribution of the three catalysts. It was found that the phthalate type internal donor strongly broadens the active center distribution by increasing the active centers in the high molecular weight fractions and depressing those in the low molecular weight side. The ether type ID increases the number of active centers in the low molecular weight side, and reduce the intrinsic activity of the centers in the high molecular side. Mechanism of the internal donor effects and the structural features of different type of active centers were discussed based on the results.

References